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A COMPARATIVE EVALUATION OF LONG-CHAIN QUATERNARY AMINES AS EXTRACTANTS OF GOLD FROM CYANIDE LEACH SOLUTIONS

P.A. Riveros
Visiting Fellow, NSERC
Extractive Metallurgy Laboratory

May, 1988

Project: 30.61.02
Gold

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57pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 88-68 (IR)

MICROMEDIA

A COMPARATIVE EVALUATION OF LONG-CHAIN QUATERNARY AMINES AS EXTRACTANTS OF GOLD FROM CYANIDE LEACH SOLUTIONS

P.A. Riveros*

Abstract

The extraction of gold from cyanide solutions with long-chain quaternary amines was studied at the bench scale and in a small continuous circuit. The use of an aromatic diluent, such as Solvesso 150, was found to be essential to prevent the formation of emulsions. Long-chain quaternary amines exhibited better selectivity for gold and faster kinetics than strong-base resins. Because of their high loading capacity for gold, low water solubility, and moderate sensitivity to the ionic strength of the aqueous phase, quaternary amines appear to be a better alternative than other liquid extractants for an industrial application. The highest potential of quaternary amines may be in the recovery of gold from heavily contaminated solutions.

KEYWORDS: Gold, Cyanide, Solvent Extraction, Quaternary Amines

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*Visiting Fellow, NSERC, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario, K1A OG1.

ÉVALUATION COMPARATIVE DE LA PERFORMANCE DES AMINES QUATERNAIRES À LONGUE CHAÎNE, EMPLOYÉES POUR EXTRAIRE L'OR DES SOLUTIONS LIXIVIANTES CYANURÉES

P.A. Riveros*

Résumé

On a étudié à l'échelle du laboratoire et dans un circuit continu de petite dimension, l'extraction de l'or au moyen d'amines quaternaires à longue chaîne à partir de solutions cyanurées. On a constaté qu'il était essentiel d'employer un diluant aromatique comme le Solvesso 150, pour empêcher la formation d'émulsions. Les amines quaternaires à longue chaîne ont manifesté une plus forte affinité pour l'or et une plus grande rapidité de réaction que les résines à forte basicité. En raison de leur forte capacité d'emmagasinement de l'or, de leur faible solubilité dans l'eau, et de leur sensibilité modérée à la force ionique de la phase aqueuse, les amines quaternaires semblent mieux convenir que les autres produits liquides d'extraction aux applications industrielles. Il semblerait que les amines quaternaires conviennent particulièrement à la récupération de l'or à partir de solutions fortement contaminées.

MOTS-CLÉS : Or, cyanure, extraction par solvant, amines quaternaires

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*Chercheur en visite, Conseil de recherche en sciences naturelles et en génie (CRSNG), Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, 555 rue Booth, Ottawa, Ontario, K1A 0G1.

1. INTRODUCTION

The extraction of gold cyanide complex with long-chain amines has previously been studied [1]. The reaction can be described, in the case of quaternary amines, as follows:

$$R_4N^+X^- + Au(CN)_2^- = R_4N^+Au(CN)_2^- + X^- \quad (1)$$

where X^- is usually Cl^- or HSO_4^-.

Despite their high affinity for the gold cyanide complex, quaternary amines have not been tested beyond the bench scale. The main reason for this is that a strong tendency to emulsification has been observed when the organic comes in contact with an alkaline solution [2,3]. This phenomenon is probably related to the surfactant properties of organic amines. Although several modifiers have been tested in the past, the diluents have been invariably of the aliphatic type [3].

Shivrin et al. [2] established that the tendency to emulsification increases as the length of the hydrocarbon chains attached to the amine group decreases. This phenomenon was attributed to the increase in water solubility of the amines with shorter chains. Amines with long hydrocarbon chains presented a lesser degree of emulsification but they had a lower loading capacity. Therefore, the most adequate chain lengths were found to be: $R=C_8$ for the amines of the type $R_4N^+X^-$ and $R=C_8$-C_{10} for

the amines of the type $R_3(CH_3)N^+X^-$. However, even under the best conditions, concentrations of 30% decanol were necessary in order to diminish the tendency to form emulsions.

Groenewald [3] found that the use of di-isobutyl ketone (DIBK) as a modifier was significantly more efficient to reduce emulsification than the long chain alcohols used by previous researchers. Although the use of DIBK enabled Groenewald to gather important information on the extraction and stripping properties of quaternary amines, the relatively high water solubility of DIBK would preclude its use on an industrial scale.

In recent years, much interest has been generated by reports on the application of phosphorus compounds as modifiers for tertiary amines in the recovery of gold [4,5]. Some of these phosphorus compounds have also been found to have extracting properties [6,7].

The Canada Centre for Mineral and Energy Technology (CANMET) is presently attempting to develop a solvent extraction system that can be applied directly to the extraction of gold from leaching pulps. The objective is to avoid the costly solid/liquid separation step and, thus, to provide a viable alternative to the carbon-in-pulp and resin-in-pulp processes. A preliminary stage in this project has been to identify a gold extractant that may be suitable for the eventual development of a solvent-in-pulp

process. For this purpose, various liquid extractants were tested with clarified solutions. Quaternary amines were found to have the best overall characteristics among all the liquid extractants tested. The emulsification problems were prevented by using an aromatic diluent (Solvesso 150). Consequently, high organic concentrations of quaternary amines could be used which, in turn, led to gold loadings that are significantly higher than those reported for other liquid extractants.

This report summarizes the results obtained with three quaternary amines (Aliquat 336, Adogen 481 and Adogen 483) and two clarified cyanide solutions from Campbell Red Lake and Teck-Corona Hemlo Mines. The experimental data obtained on a bench scale were confirmed and expanded by running a small continuous circuit. The loaded gold was recovered by stripping with acidic thiourea and air sparging or by incinerating the organic solvent.

2. EXPERIMENTAL

Aliquat 336 (Henkel Corp.) is a tri-(C_8-C_{10})alkyl methyl ammonium chloride. Adogen 481 and Adogen 483 (Sherex Chemical Company Inc.), are tri-octyl methyl ammonium chloride and tri-tridecyl methyl ammonium chloride, respectively. These three extractants were diluted with Solvesso 150, an aromatic diluent available from Exxon. The organic solutions were washed with aqueous solutions of NaCl several times before using.

Clarified cyanide solutions were obtained from Campbell Red Lake and Teck-Corona Hemlo Mines. Analyses of these solutions are presented in the next section.

The strong-base resins Amberlite IRA-400 (Rohm and Haas), Dowex MSA-2 (Dow Chemical) and Duolite A101D (Diamond Shamrock) were also tested for comparison purposes. These resins were washed several times with water before using.

Equilibrium tests were done in separatory funnels (shake-out tests). Selectivity was studied by contacting a given volume of the organic phase with successive volumes of the feed solution. The procedure was as follows: one aliquot of organic (initially 50 mL) was shaken for 10 minutes at room temperature with an aliquot of aqueous feed solution at an A/O volume ratio of 40/1. After phase disengagement both the organic and the raffinate were sampled and analyzed. This procedure was repeated several times using the same organic and fresh aqueous solution.

In the case of resins, the aqueous-to-resin ratio was 100/1 and the contact time was about six hours. The raffinates were analyzed and the resin loading was calculated by difference. Since a shrinking of the resin volume was observed as it was loaded with cyano complexes, the resin loadings are expressed as grams of metal per liter of wet settled resin in the chloride

form. A few resin samples were digested in acid and the solutions were analyzed to provide a check on the results.

The analysis of the aqueous solutions was done by inductively coupled plasma spectrophotometry. The organic solutions were analyzed directly by an X-Ray fluorescence technique.

3. RESULTS AND DISCUSSION

3.1 Extraction from the Campbell Red Lake Solution

Figure 1 presents the stagewise saturation of a 5% solution of Aliquat 336 in Solvesso 150 with successive contacts of a cyanide solution from Campbell Red Lake. This feed solution had 10 ppm of gold and significant amounts of copper, zinc, nickel and iron. The composition of this solution is shown in Table 1.

TABLE 1. Composition of the Campbell Red Lake Solution (mg/L)

Au	Cu	Fe	Ni	Zn	Ag	Co	As	Sb	Ca
10	85	31	43	34	1.2	2.1	3.3	1.8	27

It can be seen that Aliquat 336 exhibits distinct selectivity trends. Gold is extracted in larger amounts than copper, iron, and nickel despite having a lower concentration than those base metals in the feed solution. Only the loading of zinc is high, although it is proportionally lower than that of gold with

respect to their concentrations in the feed solution. The distribution coefficients, which are presented in Table 2, clearly reflect a selectivity for gold over the base metals.

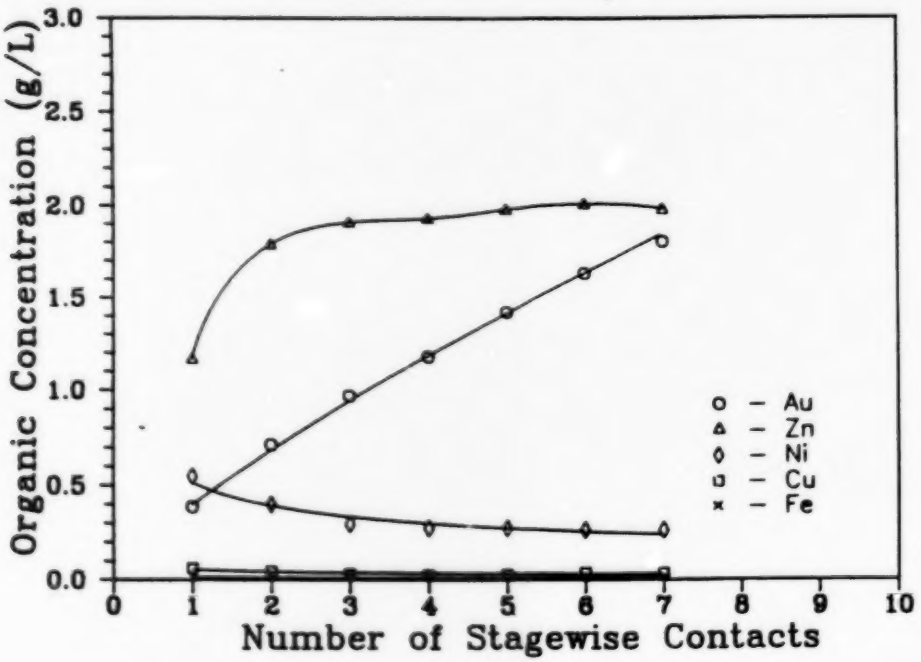

FIGURE 1. Stagewise saturation of 5% Aliquat 336 in Solvesso 150 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 40/1.

TABLE 2. Distribution Coefficients of Metal Cyano Complexes. 5% Aliquat 336 in Solvesso. Feed: Campbell Red Lake

Contact	Au	Cu	Fe	Ni	Zn
1	350.0	0.9	0.6	21.9	191.8
2	255.7	0.7	0.6	9.3	81.4
3	236.8	0.5	0.9	7.4	65.9
4	222.6	0.4	0.6	6.9	58.5
5	229.0	0.4	0.6	6.9	58.2
6	229.6	0.6	0.6	6.6	59.1
7	233.8	0.5	0.6	6.6	58.2

As a way to ascertain the reversibility of the ion exchange, the saturation experiment was repeated with an organic solution initially loaded with zinc cyanide complex. Figure 2 shows that after a sufficient number of contacts the same loadings are obtained as in the previous experiment. This result also confirms the selectivity of Aliquat 336 for gold over zinc and the other base metals.

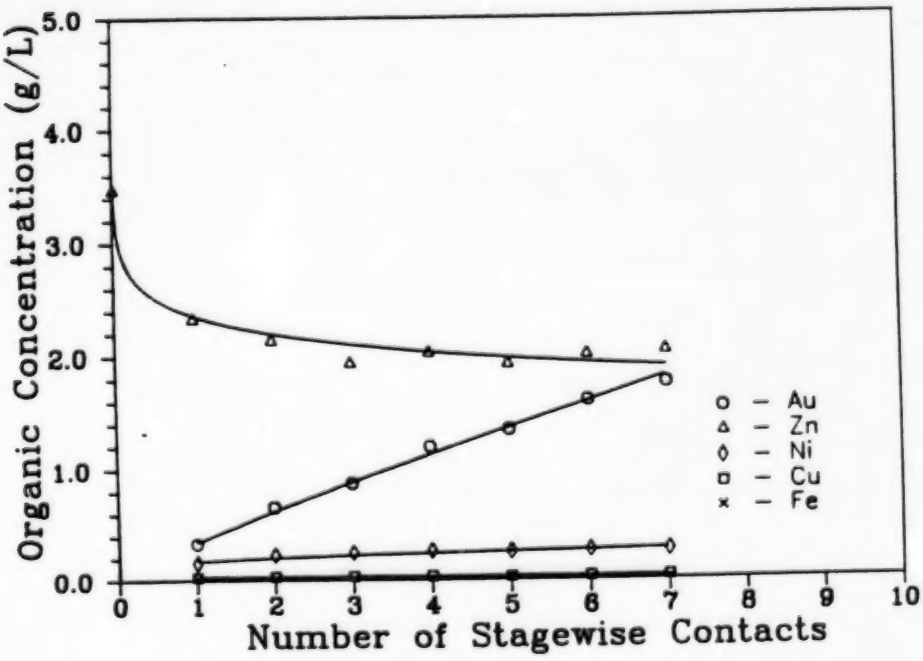

FIGURE 2. Stagewise saturation of 5% Aliquat 336 (initially loaded with zinc cyanide complex) in Solvesso 150 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 40/1.

The stagewise saturation experiments were repeated with two quaternary amines from a different source. Figures 3 and 4 present the results obtained with 5% solutions of Adogen 481 and Adogen 483 in Solvesso 150. Despite having slightly lower loading capacities, the Adogen reagents showed the same selectivity trends of Aliquat 336. At saturation, the distribution coefficients of gold for Adogen 481 and Adogen 483 were 177 and 140 respectively. Adogen 483 exhibited the highest selectivity for gold but the lowest loading capacity. Adogen 481 behaved similarly to Aliquat 336, except that a third phase formed at high loadings. This could be prevented, however, by adding isodecanol. The phase separation was fast in all cases and no signs of emulsification were observed.

The marked selectivity for gold exhibited by the quaternary amines is rather surprising since these reagents are chemically related to the strong base resins which are known to extract indiscriminately a large number of metal cyanide complexes [8]. Therefore, with the purpose of comparison, three common strong base resins (Amberlite IRA-400, Dowex MSA-2 and Duolite A101D) were tested under the same conditions as the preceding experiments. Figures 5, 6 and 7 present the stagewise saturation of these resins. It is apparent from these figures that, unlike

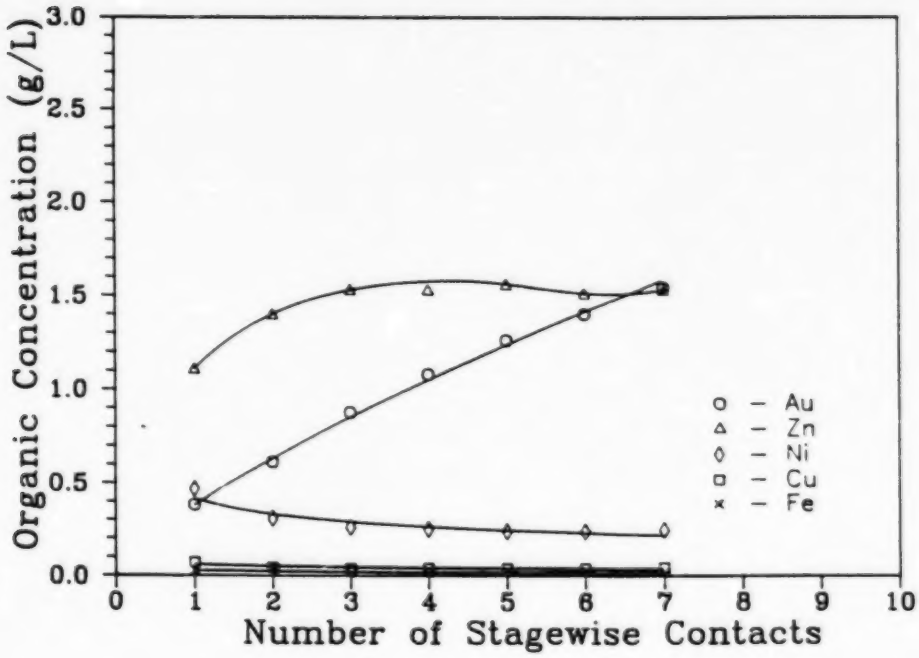

FIGURE 3. Stagewise saturation of 5% Adogen 481 and 2% isodecanol in Solvesso 150 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 40/1.

quaternary amines, the strong base resins exhibited no selectivity for gold since larger amounts of iron, copper, zinc and nickel were also extracted. The distribution coefficients of the major metals, obtained during the extraction with Amberlite IRA-400, are presented in Table 3. Similar values were obtained for Dowex MSA-2 and Duolite A101D.

The lack of selectivity for gold of Amberlite IRA-400 (and the other two strong base resins) is apparent from the distribution coefficients. All metals, except copper, are extracted in

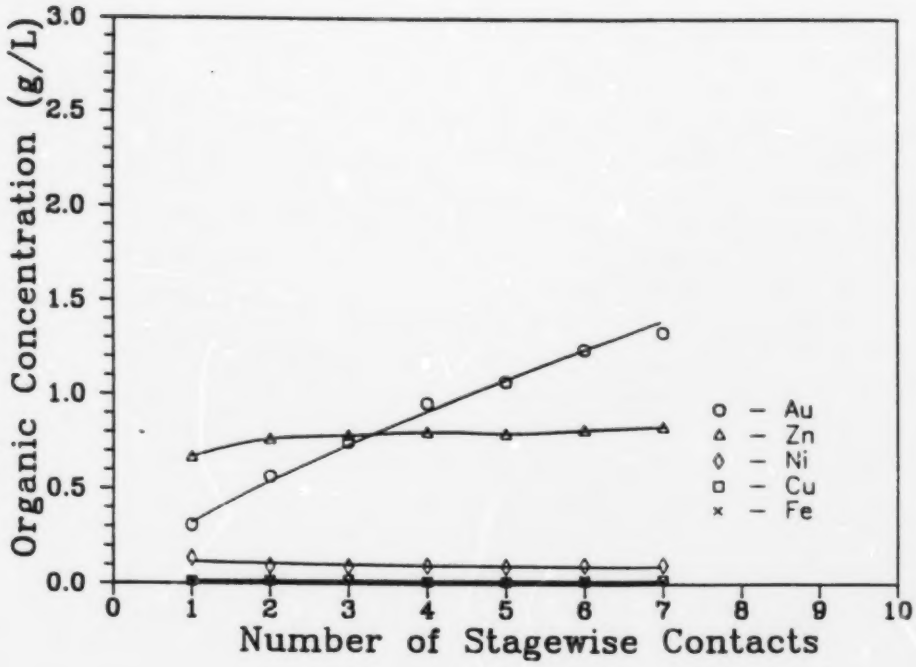

FIGURE 4. Stagewise saturation of 5% Adogen 483 in Solvesso 150 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 40/1.

TABLE 3. Distribution Coefficients of Metal Cyano Complexes. Amberlite IRA-400. Feed: Campbell Red Lake solution

Contacts	Au	Cu	Fe	Ni	Zn
1	3233	23900	24900	39900	32900
2	479	364	540	1437	2536
3	287	125	168	537	1203
4	221	99	149	388	663
5	203	85	133	351	672
6	175	81	148	310	542
7	166	73	139	304	579
8	157	73	144	287	537
9	148	67	135	285	559

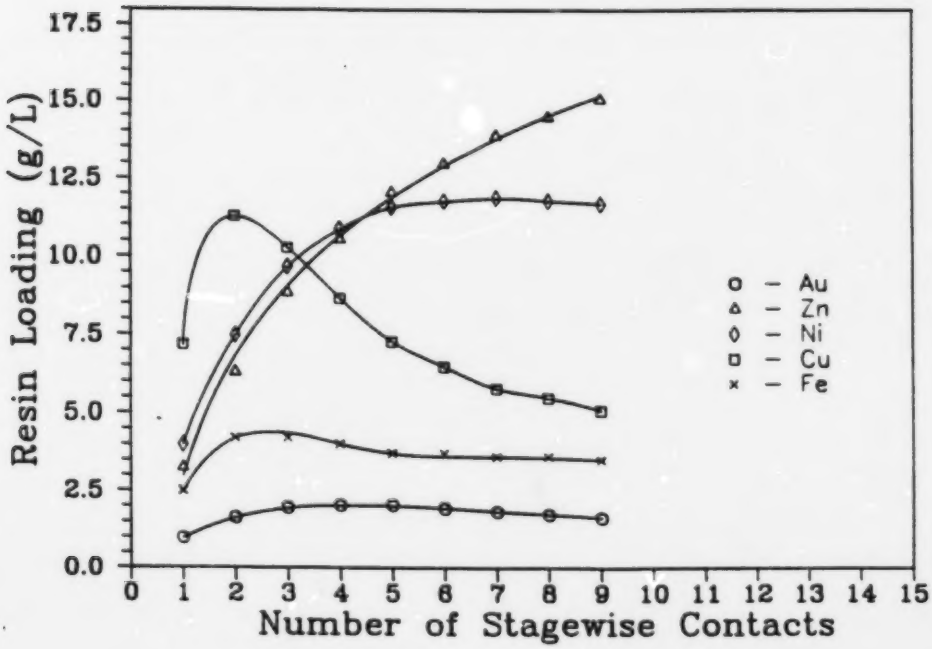

FIGURE 5. Stagewise saturation of Amberlite IRA-400 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 100/1.

either equivalent or larger amounts than gold. The different behaviour of quaternary amines and strong base resins is clearly shown by the separation factors (calculated from the last set of distribution coefficients) that are presented in Table 4.

TABLE 4. Separation Factors. Feed: Campbell Red Lake solution

Extractant	Au/Cu	Au/Zn	Au/Ni	Au/Fe
5% Aliquat 336	455.2	4.0	35.7	389.6
5% Adogen 481	306.8	4.2	29.9	306.8
5% Adogen 483	474.8	6.1	56.3	227.5
Amberlite IRA-400	2.2	0.3	0.5	1.1
Dowex MSA-2	4.3	0.5	0.8	1.5
Duolite A101D	2.0	0.2	0.4	1.0

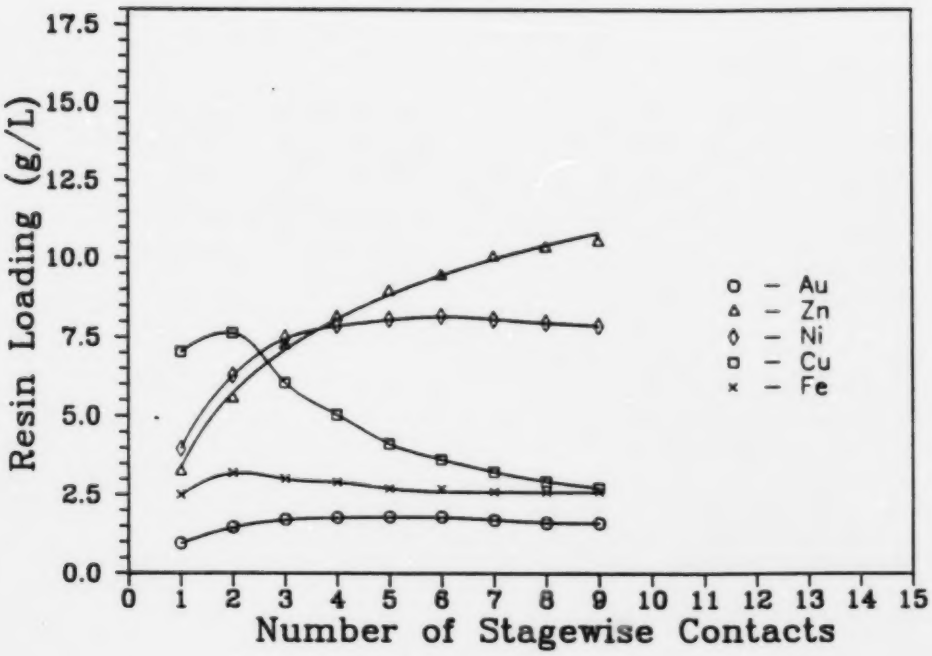

FIGURE 6. Stagewise saturation of Dowex MSA-2 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 100/1.

The selectivity exhibited by the quaternary amines is in qualitative agreement with the results obtained by Irving and Damodaran who found that a quaternary amine dissolved in hexone did not extract iron or copper cyanides [16]. However, the marked difference in selectivity between quaternary amines and resins is rather surprising considering that the active group in both cases is basically the same, i.e., a quaternary ammonium ion. Shivrin et al. [2] suggested that the selectivity for gold of quaternary amines appears to be related to the configuration of the amino group. According to these researchers, $R_4N^+X^-$ and

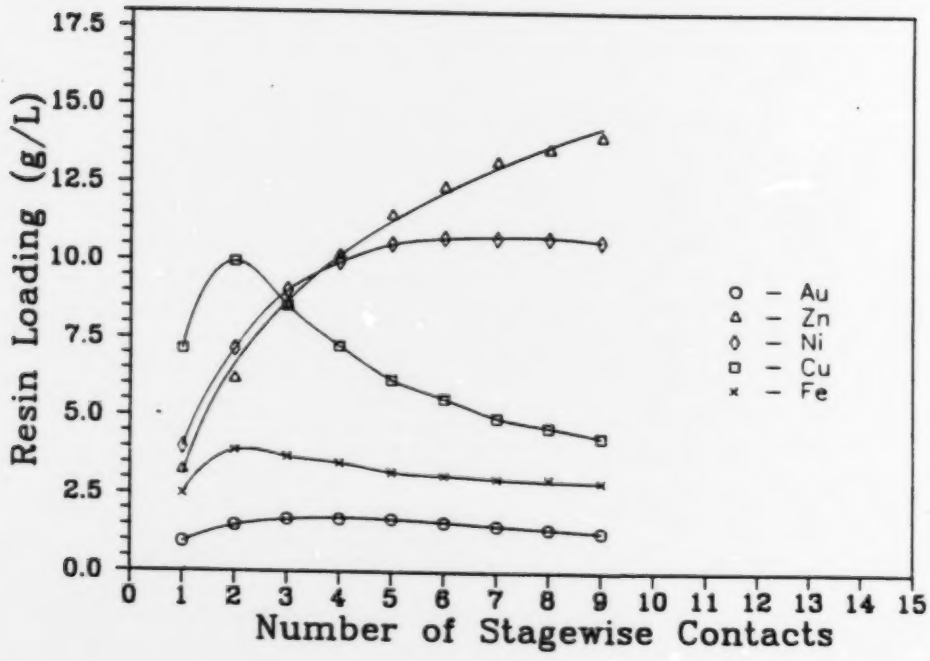

FIGURE 7. Stagewise saturation of Duolite A101D with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 100/1.

$R_3(CH_3)N^+X^-$ possess a higher selectivity for gold than the quaternary amines of the type $R_2(CH_3)_2N^+X^-$ or $R(CH_3)_3N^+X^-$. The fact that the amines used in the present work (Aliquat 336, Adogen 481 and Adogen 483) belong to the first category of amines, i.e., $R_3(CH_3)N^+X^-$, is in agreement with their hypothesis. By contrast, Amberlite IRA-400 and Duolite A101D have a configuration of the type $R(CH_3)_3N^+X^-$ and are, therefore, more closely related to the less selective family of quaternary amines.

It is interesting to note that Dowex MSA-2, which has a $CH_3CH_2OH^-$ group (in addition to two methyl groups) attached to the amino group, shows a slightly better selectivity for gold than the other two resins. Furthermore, Adogen 483, which has the longest hydrocarbon chains (tridecyl), exhibits a higher selectivity for gold than the other quaternary amines as indicated by the separation factors. Therefore, both the number and the length of the hydrocarbon chains attached to the amino group appear to exert an important influence on the selectivity for gold. Those amino groups bonded to the more and longest hydrocarbon chains exhibit the highest selectivity while those bonded mainly to methyl groups exhibit the poorest selectivity.

3.1.1 Loading capacity

Figure 8 presents the distribution isotherms between the Campbell Red Lake solution and the following extractants: Amberlite IRA-400, Dowex MSA-2, Duolite A101D and Aliquat 336 in concentrations of 5, 10 and 20% in Solvesso 150. From this figure it can be predicted that, with the appropiate number of stages, a 5% Aliquat 336 solution will produce the same gold loading as the strong base resins. Significantly higher loadings can be obtained with 10 and 20% Aliquat 336 solutions. Since the quaternary amines also exhibit faster reaction kinetics than the resins, the organic inventory, surge capacity and volumetric transportation requirements of a solvent extraction process would be smaller, leading to capital cost savings.

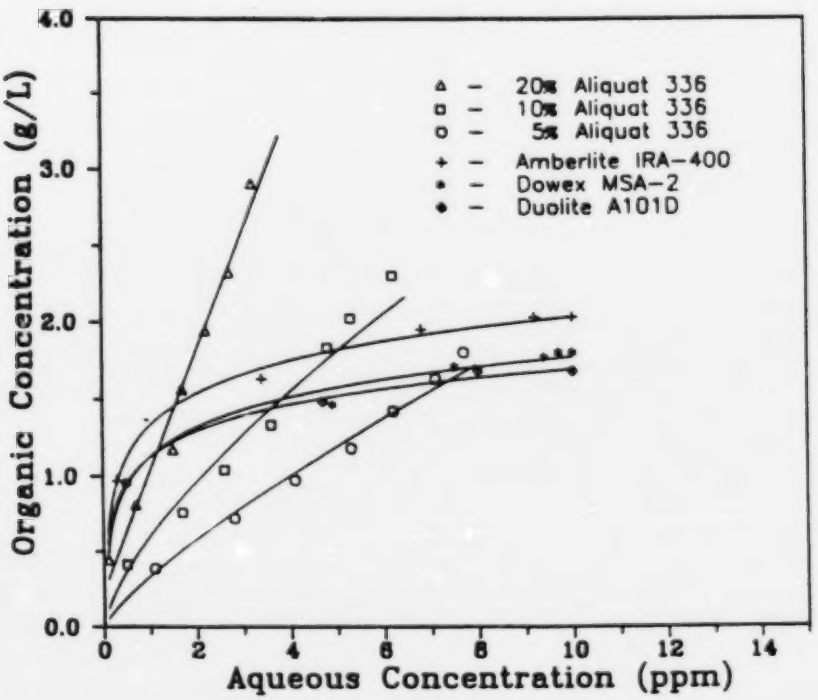

FIGURE 8. Gold extraction isotherms for various extractants with a Campbell Red Lake solution.

Figure 9 presents the stagewise saturation of a 20% solution of Aliquat 336 in Solvesso 150 with the Campbell Red Lake solution. This experiment was done to demonstrate that high concentrations of quaternary amines in Solvesso 150 can be used without emulsification problems. By contrast, Groenewald reports that concentrations over 4% Aliquat 336 in kerosene, even in the presence of 30% DIBK as modifier, led to emulsion formation [3]. The possibility of using a high concentration of quaternary amine leads to exceptionally high gold loadings and distribution coefficients. It can be seen from the graphs that a 20% Aliquat 336

solution produced gold loadings of more than 3 g/L and distribution coefficients close to 1000. These values are considerably higher than those of other liquid extractants. As a reference, the gold distribution coefficients of 100% TBP and a 1:1 mixture of TBP/Alamine 336 were 8.4 and 30.1 respectively when tested on the unmodified Campbell Red Lake solution [9]. J.D. Miller et al. [6] reported gold distribution coefficients of 17 to 155 for DBBP and 6 to 55 for TBP using synthetic solutions. Groenewald obtained a gold loading of 0.52 g/L using Aliquat 336 diluted in kerosene/DIBK and a synthetic gold solution [3].

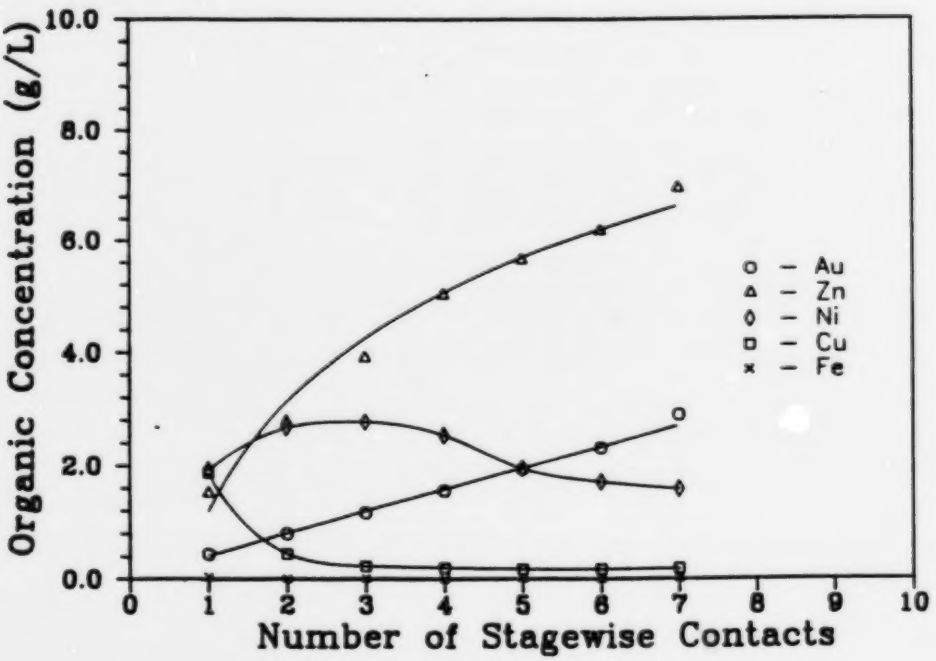

FIGURE 9. Stagewise saturation of 20% Aliquat 336 in Solvesso 150 with a Campbell Red Lake solution. The aqueous-to-organic volume ratio at each stage was 40/1.

3.1.2 Effect of ionic strength

The ionic strength has been reported to have a strong influence on the extractive properties of some phosphorus compounds such as TBP [7]. In order to study this effect, enough sodium nitrate was added to the Campbell Red Lake solution to make the concentration 1 M $NaNO_3$. Figure 10 presents the stage-wise saturation of a 5% solution of Aliquat 336 with the modified cyanide solution. The high ionic strength of the aqueous phase reduces strongly the extraction of the base metals whereas the extraction of gold is affected to a much lesser degree. The distribution coefficients presented in Table 5 corroborate this observation.

TABLE 5. Distribution Coefficients. 5% Aliquat 336.
Feed: Campbell Red Lake + 1M $NaNO_3$

Contact	Au	Cu	Fe	Ni	Zn
1	180.0	0.0	0.0	2.2	35.6
2	160.0	0.0	0.0	1.0	26.7
3	149.5	0.0	0.0	0.0	23.5
4	165.1	0.0	0.0	0.0	23.5
5	154.7	0.0	0.0	0.0	18.4
6	164.6	0.0	0.0	0.0	20.0
7	167.1	0.0	0.0	0.0	21.8

The extraction of metal cyanide complexes from the Campbell Red Lake at 1 M $NaNO_3$ solution by Amberlite IRA-400 is presented in Figure 11. As in the previous case, the ionic strength has a much stronger depressing effect on the extraction of base metals than on the extraction of gold. This differential effect can be clearly seen from the distribution coefficients presented in Table 6.

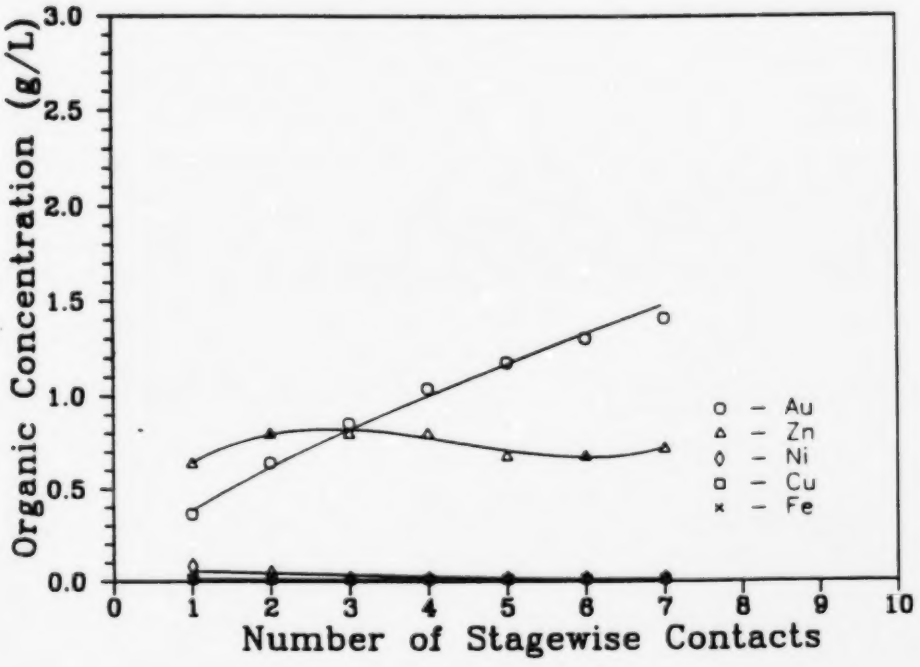

FIGURE 10. Stagewise saturation of 5% Aliquat 336 in Solvesso 150 with a Campbell Red Lake solution containing 1 M $NaNO_3$. The aqueous-to-organic volume ratio at each stage was 40/1.

TABLE 6. Distribution Coefficients. Amberlite IRA-400. Feed: Campbell Red Lake + 1M $NaNO_3$

Contacts	Au	Cu	Fe	Ni	Zn
1	358.3	20.6	4.0	200.0	476.3
2	221.3	15.6	3.8	140.7	314.0
3	210.1	11.4	3.8	126.5	268.6
4	181.6	10.4	3.8	110.3	232.5
5	193.9	10.5	3.8	110.3	241.7
6	177.8	9.1	8.0	100.0	225.3
7	196.1	6.4	12.0	105.1	242.3

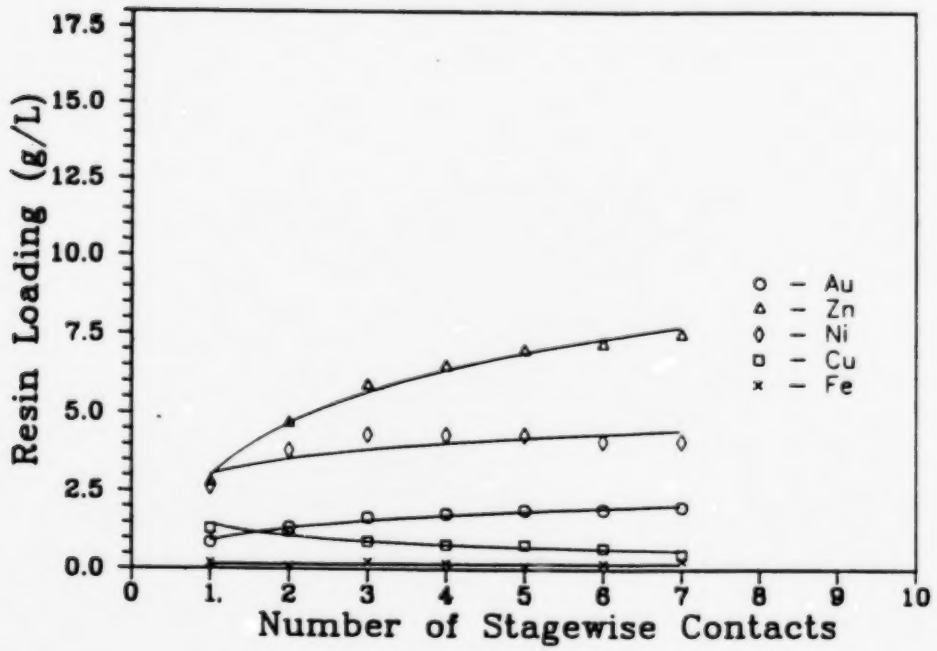

FIGURE 11. Stagewise saturation of Amberlite IRA-400 with a Campbell Red Lake solution containing 1 M $NaNO_3$. The aqueous-to-organic volume ratio at each stage was 100/1.

Figure 12 shows the effect of sodium nitrate on the gold distribution isotherms of Amberlite IRA-400 and 5% Aliquat 336. The depressing effect of the high ionic strength on the gold extraction is seen to be larger for Amberlite IRA-400 than for Aliquat 336. However, in both cases the extraction of gold is still high. These results indicate that the extraction of gold by quaternary amines is only moderately sensitive to the ionic strength of the aqueous phase. The selectivity for gold, however, can be significantly increased at a high ionic strength.

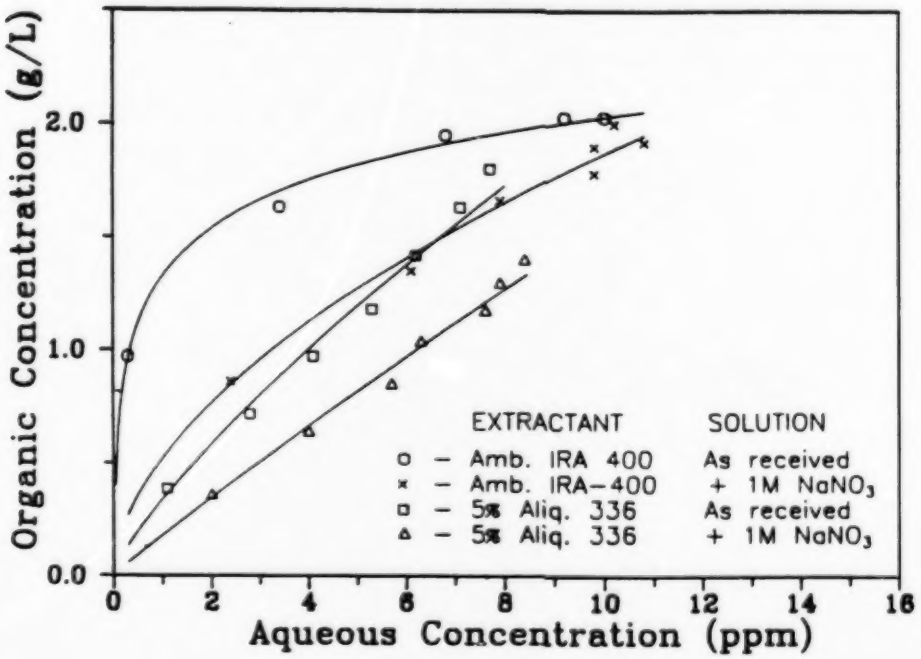

FIGURE 12. Effect of the ionic strength on the gold extraction isotherms.

Since it is also known that variations in the pH of the aqueous solution do not have a strong effect on the extractive properties of quaternary amines [3], these extractants do not require any pre-conditioning of the feed solution prior to solvent extraction. This represents an important advantage over the newly developed extractants for gold that require either a high ionic strength [6] or a lowering of the pH of the feed solution in order to increase the efficiency of the extraction [5].

3.2 Extraction from the Teck-Corona Hemlo Solution

The previous experiments were done with a solution that had a high concentration of gold but that was heavily contaminated with base metals. It was decided to compare the performance of quaternary amines with a different cyanide solution which was obtained from Teck-Corona Hemlo Mines. This solution had a lower gold concentration but it was much less contaminated with base metals as shown in Table 7. An important difference is that the concentration of zinc is very low in this solution.

TABLE 7. Feed Solution from Teck-Corona Hemlo Mines (ppm)

Au	Cu	Fe	Ni	Zn	Ag	Co	As	Sb	Ca
6	4.7	14	1.5	0.2	0.17	0.1	0.3	2.3	115

Figure 13 presents the stagewise saturation of a 2.5% solution of Aliquat 336 in Solvesso 150 with the Teck-Corona Hemlo solution. It can be seen that the loading of gold is significantly higher than those of the other metals present in the cyanide solution. There is also an increase in the loadings of nickel, iron and copper as compared to those observed with the Campbell Red Lake solution. This effect is probably due to the absence of the zinc cyanide complex and the lower ionic strength of the Teck-Corona Hemlo solution.

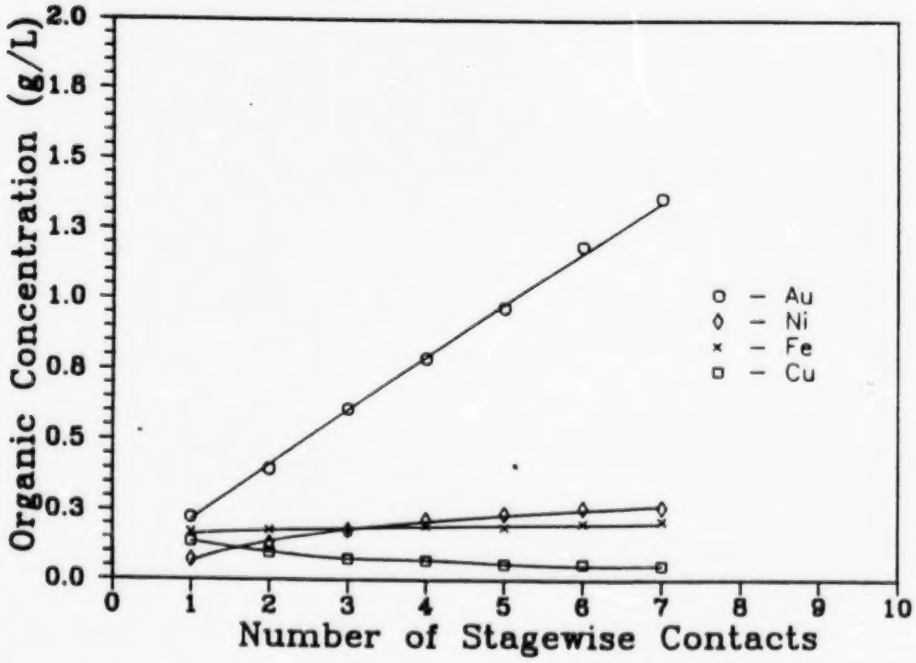

FIGURE 13. Stagewise saturation of 2.5% Aliquat in Solvesso 150 with a Teck-Corona Hemlo solution. The aqueous-to-organic volume ratio at each stage was 40/1.

Table 8 presents the distribution coefficients obtained during the stagewise saturation of a 5% Aliquat 336 solution in Solvesso 150. By comparison with the Campbell Red Lake solution, there is a significant increase (1 order of magnitude) in the gold distribution coefficients. The distribution coefficients of nickel, copper and iron are also higher than before.

TABLE 8. Distribution Coefficients of Metal Cyano Complexes. Feed: Teck-Corona Hemlo. 5% Aliquat 336

Contact	Au	Cu	Fe	Ni
1	10850.0	2180.0	90.7	3750.0
2	19800.0	199.3	8.4	7250.0
3	12260.0	50.2	11.6	1970.0
4	2684.4	40.4	16.7	2690.0
5	2666.7	38.8	19.6	1750.0
6	2708.3	30.8	23.2	1340.0
7	2539.7	27.3	27.6	1210.0

Figure 14 shows the stagewise saturation of Amberlite IRA-400 with the Teck-Corona Hemlo solution. The same experiment was also carried out with Dowex MSA-2 and similar results were obtained. Due to the relatively low metal concentrations of the Hemlo solution, the maximum loading capacity was not attained after 10 contacts (1000 Bed Volumes). However, it can be seen that, as before, no selectivity is observed since all the main metals are extracted in amounts that are proportional to their aqueous concentrations. The distribution coefficients, which are presented in Table 9 indicate large increases with respect to the values obtained with the Campbell Red Lake solution.

It is apparent that the presence and concentration of other metal cyanides is the factor having the most effect on the extraction of gold by quaternary amines and strong base resins. Much higher gold distribution coefficients are observed in the extraction from dilute less-contaminated solutions, such as the Teck-Corona Hemlo, although the selectivity is lower. Table 10

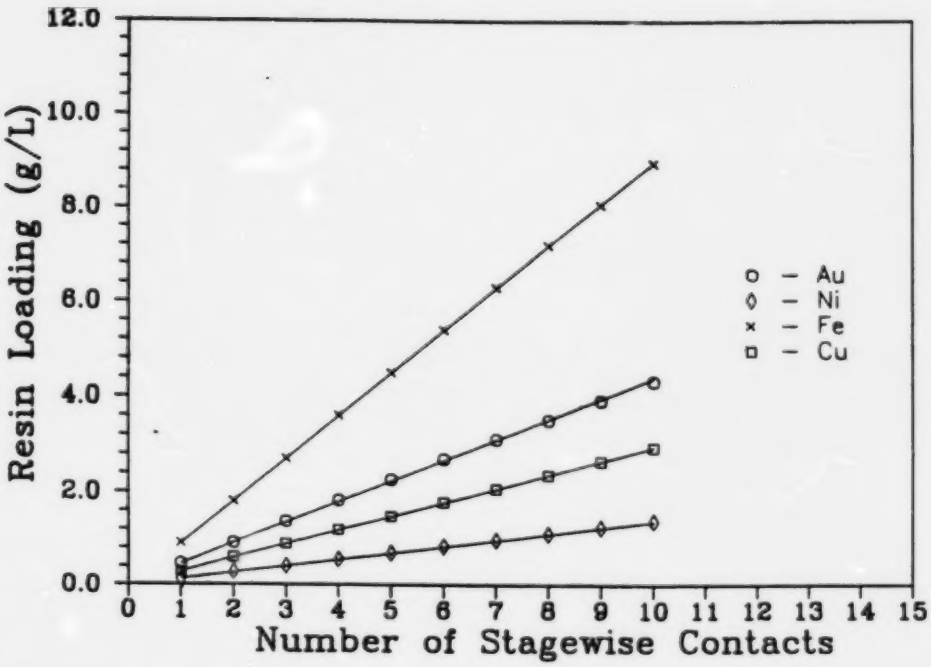

FIGURE 14. Stagewise saturation of Amberlite IRA-400 with a Teck-Corona Hemlo solution. The aqueous-to-organic volume ratio at each stage was 100/1.

TABLE 9. Distribution Coefficients of Metal Cyano Complexes. Feed: Teck-Corona Hemlo. Amberlite IRA-400

Contacts	Au	Cu	Fe	Ni
1	11400	14900	89900	6900
2	22800	19833	179800	13800
3	34200	11088	269700	20700
4	45600	59250	179750	27600
5	11320	49400	149733	34500
6	8980	59300	269500	41400
7	7785	20690	314400	48300
8	5857	39383	143660	55200
9	7848	26530	40315	62100
10	7207	29430	89530	69000

TABLE 10. Separation Factors of Various Extractants.
Feed Solution: Teck-Corona Hemlo

Extractant	Au/Cu	Au/Ni	Au/Fe
2.5% Aliquat 336	44.9	3.1	35.5
5.0% Aliquat 336	93.0	2.1	92.0
Amberlite IRA-400	0.24	0.10	0.08
Dowex MSA-2	1.36	0.22	1.13

presents the separation factors for the extractants tested with the Teck-Corona Hemlo solution. Because of the relatively higher loadings of base metals, the separation factors indicate a reduced selectivity for gold in all cases, as compared with those obtained with the Campbell Red Lake solution. This is probably related to the effect of the ionic strength on the selectivity as discussed above. Quaternary amines still exhibit better selectivity for gold than do the strong base resins.

3.2.1 Loading capacity

Figure 15 presents the distribution isotherms between the Teck-Corona Hemlo solution and the following extractants: Amberlite IRA-400, Dowex MSA-2 and Aliquat 336 in concentrations of 2.5, 5 and 10% in Solvesso 150. Due to the low concentrations of the Teck-Corona Hemlo solution, it is difficult to attain the complete saturation of the extractants. However, it is apparent that the increase in gold extraction, due to the lower contamination of the Hemlo solution, is considerably higher in the case of strong base resins. This effect is to be expected from the lack of selectivity of strong base resins. Aliquat 336 also shows a

higher loading capacity for gold from the Teck-Corona Hemlo solution but the increase is relatively smaller.

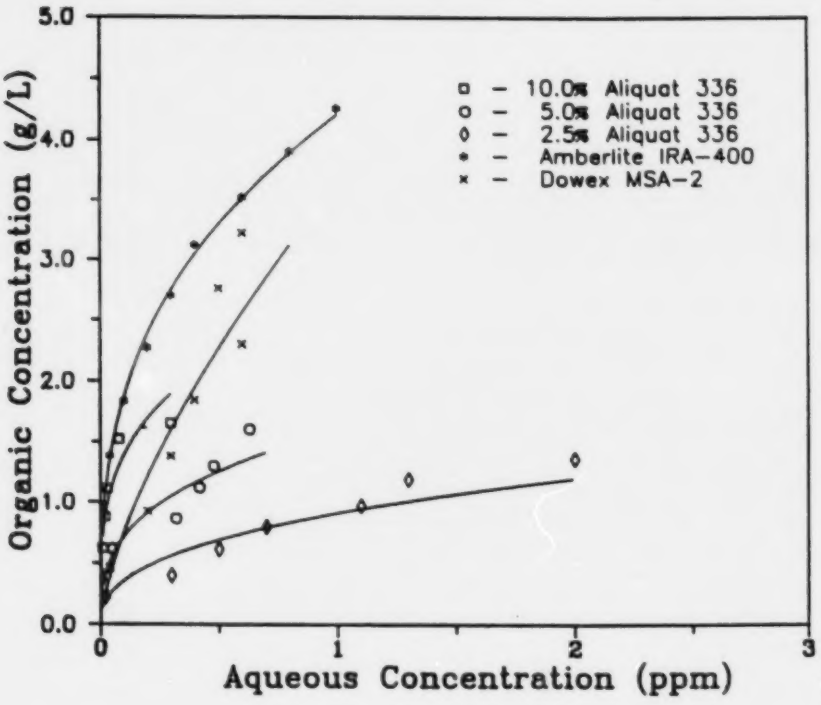

FIGURE 15. Gold extraction isotherm for various extractants with a Teck-Corona Hemlo solution.

As a corollary, it can be concluded that, because of their better selectivity for gold, quaternary amines are less sensitive than strong base resins to the presence of contaminating cyanide complexes. Therefore, they would be particularly suitable for the extraction of gold from impure cyanide solutions.

3.3 Continuous Circuit

Due to the good characteristics shown by the quaternary amines on the bench tests, it was decided to test their behaviour on a continuous circuit. The main difficulty in setting up such an experiment was to find a suitable contactor that could operate at an extremely high aqueous-to-organic flow ratio. Due to the low gold concentration in a typical feed solution (2-10 ppm) and the expected concentrations in the organic phase (2-3 gpl), A/O flow ratios in the range of 300-1000:1 become necessary. These ratios are significantly higher than those normally found in solvent extraction operations. Such a high A/O flow ratio dictates that the phase mixing should be done with an organic continuous dispersion in order to minimize the losses of organic solvent.

Most conventional contactors are not designed to handle very high A/O flow ratios. The Davy McKee CMS contactor [10] and mixer-settlers are among the few that appear suitable for this special application. A small laboratory CMS contactor was not available at the time. Mixer-settlers could be used as long as they are fitted with organic recycling lines to keep the A/O ratio in the mixer close to 1:1. However, this is complicated because of the need to control both the recycling and advancing organic flow in every stage. Besides, organic continuous dispersion is difficult to maintain if pumping/mixing impellers are used while conventional impellers have to be used in conjunction with interstage pumping.

After considering the alternatives and bearing in mind that a small organic inventory is required to keep the volume of the cyanide solution within reasonable limits, it was decided to use a series of agitated glass columns specially designed and built for this experiment. The main feature of this equipment, which is shown in Figure 16, is that the organic phase is transferred from one column to the next in a periodic and countercurrent manner (with respect to the aqueous flow). This procedure is similar in nature to the operation of ion exchange columns. The main purpose of this procedure is to avoid the need for separate organic settling areas and, consequently, to reduce the organic inventory. The columns were fitted with mechanical impellers of the pump/mixing type. By careful adjustment of the impeller speed, level controls and aqueous flow rate, it was possible to operate the columns with an organic-continuous dispersion. When this condition was attained, two liquid zones were clearly discernible within the columns. The lower three-quarters of the column were filled with settled aqueous raffinate while the top quarter corresponded to an organic-continuous dispersion zone.

During operation the aqueous solution was allowed to flow continuously by gravity through the columns. A peristaltic pump was used to introduce the cyanide solution into the top column. After the desired volume of aqueous solution had passed through the columns, the organic phase in each column was pumped to the next column in a countercurrent direction.

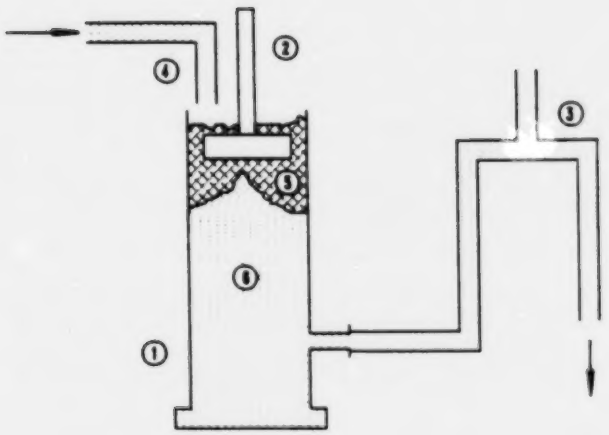
① – Extraction Column
② – Pump/Mix Stirrer
③ – Level Control (aqueous to next stage)
④ – Aqueous Feed (from previous stage)
⑤ – Organic-continuous Dispersion
⑥ – Settled Aqueous Phase

FIGURE 16. Agitation column for continuous solvent extraction of gold.

This column equipment was considered suitable for the solvent extraction of gold because of the following points:

1. There is virtually no limit to the A/O flow ratios that can be used.

2. The phase mixing is always done in the organic-continuous mode.

3. Since there are no settlers for the organic phase, the organic inventory is as small as possible.

4. Since the impeller is positioned at the top of the column there is no vortex and the agitation action is gentle. This avoids organic losses by splashing and reduces the intake of air.

5. The periodic tranfer of organic ensures the right A/O flow ratio irrespective of variations in the impeller speed or changes in the volume of the organic phase.

The continuous circuit experiment was run for 114.7 hours during which 164 L of the Campbell Red Lake solution and 180 L of the Teck-Corona Hemlo solution were processed.

Adequate experimental conditions were estimated by constructing McCabe-Thiele diagrams from the distribution isotherms shown earlier. It was determined that, for the Campbell Red Lake solution, four stages would be necessary to obtain complete extraction of gold with 10% Aliquat 336. An A/O flow ratio between 140/1 and 200/1 would be suitable. For the Teck-Corona Hemlo solution three stages with 5% Aliquat 336 would be required. An A/O ratio of 400/1 can be used. The aqueous flow rate was set at about 1 BV/min (50-60 mL/min), which gave a residence time of 2-3 minutes in each column.

Table 16 summarizes the operational data used during the continuous circuit experiment. The first data column identifies

the cycle (each time the organic was transferred a new cycle started). The second data column shows the running time for the cycle. The third column shows the flow rate of the aqueous solution. The fourth column shows the amount of fresh organic introduced into the system. The fifth column shows the amount of organic withdrawn from the system. The last column shows the A/O flow ratio over the cycle.

TABLE 16. Continuous Circuit Operation Conditions

Cycle	Running Time (h)	Aqueous Passed (L)	Aqueous Flow Rate (mL/min)	Organic In	Organic Out	A/O flow ratio
5	2.43	7	48.01	50	42	140/1
6	2.45	7	47.62	50	31	140/1
7	2.27	7	51.40	50	50	140/1
8	2.30	7	50.72	50	43	140/1
9	2.28	7	51.17	50	44	140/1
10	2.33	7	50.07	50	45	140/1
11	3.27	10	50.97	50	45	200/1
12	3.25	10	51.28	50	43	200/1
13	3.23	10	51.60	50	41	200/1
14	3.23	10	51.60	50	46	200/1
15	3.83	10	43.52	50	43	200/1
16	3.22	10	51.76	50	44	200/1
17	3.27	10	50.97	50	44	200/1
18	3.32	10	50.20	50	43	200/1
19	3.30	10	50.51	50	42	200/1
21	5.70	18	52.63	60	58	300/1
22	5.62	18	53.38	60	52	300/1
23	7.90	24	50.63	60	57	400/1
24	7.72	24	51.81	60	52	400/1
25	7.78	24	51.41	60	52	400/1
26	8.50	24	47.06	60	51	400/1
27	8.80	24	45.46	60	51	400/1
28	7.90	24	50.63	60	52	400/1

Cycles 1-19: 10% Aliquat 336 and Campbell Red Lake Solution
Cycles 20-28: 5% Aliquat 336 and Teck-Corona Hemlo Solution

Table 17 presents the ICP analysis of the raffinates collected after each cycle. With the Campbell Red Lake solution, the gold extraction can be estimated at 99.3% when the A/O flow ratio is 140/1 (cycles 6 to 10) and 98.0% when the A/O flow ratio is 200/1 (cycles 15 to 18). With the Hemlo solution the gold extraction was 98.6% when the A/O flow ratio was 400/1 (cycles 23 to 28).

TABLE 17. Continuous Circuit. Analysis of Raffinates (mg/L)

Cycle	Volume (L)	Au	Cu	Zn	Ni	Fe
5	7	<0.04	86	4	44	25
6	7	0.05	83	7	43	30
7	7	0.06	85	11	41	31
8	7	0.06	85	11	42	32
9	7	0.10	85	12	41	31
10	7	0.08	84	12	40	31
15	10	0.20	81	19	40	30
16	10	0.20	78	19	41	31
17	10	0.20	78	19	41	31
18	10	0.20	79	19	40	30
23	24	0.04	4	0	0	14
24	24	0.10	5	0	0	14
25	24	0.10	5	0	0	14
26	24	0.08	5	0	0	14
27	24	0.10	4	0	0	14
28	24	0.10	5	0	0	14

Cycles 1-19: 10% Aliquat 336 and Campbell Red Lake Solution
Cycles 20-28: 5% Aliquat 336 and Teck-Corona Hemlo Solution

The X-Ray fluorescence analyses of the organic extracts are presented in Table 18.

The total amount of gold in the organic solutions collected when the A/O flow ratio was 140/1 (cycles 6 to 10) was 346.4 mg which corresponds to 99.0% of the total amount of gold passed through the columns. This is almost exactly the gold extraction

TABLE 18. Continuous Circuit. Analysis of Organics (mg/L)

Cycle	Vol.(mL)	Au	Cu	Zn	Ni	Fe
5	42	1610	102	3370	521	48
6	31	2100	113	3670	588	52
7	50	1460	100	3410	524	47
8	43	1480	98	3220	504	42
9	44	1620	103	3420	533	45
10	45	1630	102	3560	561	45
11	45	1920	72	3600	536	<30
12	43	1990	68	3460	504	<30
13	41	2130	69	3640	536	<30
14	46	1970	72	3580	535	<30
15	43	2130	71	3600	539	<30
16	44	2050	65	3520	507	<30
17	44	2110	63	3570	528	<30
18	43	2300	76	3820	557	<30
19	42	2110	77	3560	541	<30
21	58	1560	43	146	473	<30
22	52	1710	53	261	592	<30
23	57	2200	54	323	699	<30
24	52	2510	56	124	736	<30
25	52	2570	61	98	736	<30
26	51	2540	60	104	742	<30
27	51	2680	67	100	750	<30
28	52	2580	82	90	733	<30

Cycles 1-19: 10% Aliquat 336 and Campbell Red Lake Solution
Cycles 20-28: 5% Aliquat 336 and Teck-Corona Hemlo Solution

estimated from the raffinates. A similar calculation when the A/O flow ratio was 200/1 (cycles 15 to 19) shows that the total amount of gold in the organic solutions was 462.15 mg which corresponds to 94.3% of the total amount of gold passed through the columns. For the Teck-Corona Hemlo solution and an A/O flow ratio of 400/1 (cycles 23 to 28), the amount of gold recovered was 789.9 mg or 91.4% of the total gold passed through the columns. These recoveries, which are still subject to optimization, are comparable with typical recoveries reported for Merrill-Crowe and activated carbon processes [17].

The results of the continuous circuit are in agreement with the bench tests and they confirm the ability of Aliquat 336 to extract gold efficiently and selectively from cyanide solutions in a multi-stage countercurrent system. This experiment also demonstrates the feasibility of a continuous solvent extraction process for gold. Virtually no operational problems were encountered. Small amounts of crud were observed when the organic phase was highly loaded but this did not accumulate or interfere with the extraction. The same results were obtained with Aliquat 336 in the chloride and in the sulphate form. The good phase separation observed in all cases is an attractive feature of quaternary amines because other extractants for gold usually exhibit a tendency to form emulsions [15].

X-Ray fluorescence analysis of the loaded organic solutions had shown the absence of heavy elements other than the ones discussed above. By contrast, X-Ray fluorescence analyses of loaded Amberlite IRA-400 detected, in addition to the main metals, trace amounts of cobalt, silver and arsenic. With the purpose of verifying the first result, some of the raffinate solutions were analyzed for other metals that may be of importance in the metallurgy of gold. The results are presented, along with the feed concentrations, in Table 19.

The analyses of the raffinates confirm that none of the other elements, namely, cobalt, silver, arsenic, calcium and

TABLE 19. Continuous Circuit. Analysis of other metals (mg/L)

Cycle or Feed Soln.	Volume (L)	Ag	Co	As	Sb	Ca
Campbell	--	1.2	2.1	3.3	1.8	27
9	7	1.1	2.1	3.0	1.7	27
10	7	1.1	2.1	2.8	1.6	27
16	10	1.2	2.1	3.4	2.0	22
17	10	1.2	2.1	3.1	1.6	21
Hemlo	--	0.17	0.1	0.3	2.3	115
27	24	0.14	0.1	0.0	2.3	130
28	24	0.14	0.1	0.0	2.3	127

Cycles 1-19: 10% Aliquat 336 and Campbell Red Lake Solution
Cycles 20-28: 5% Aliquat 336 and Teck-Corona Hemlo Solution

antimony were extracted to a significant extent. Unfortunately, silver was present in very low concentrations in both solutions and, therefore, the extraction of this metal could not be studied in detail. These results underline the fact that quaternary amines can exclude many elements from the final product. This fact could well result in an effective reduction of the subsequent refining steps.

The concentrations of free cyanide, thiocyanate and dissolved amine were monitored throughout the experiment. Some typical values are presented in Table 20.

Although quaternary amines are known to have affinity for the cyanide ion and the thiocyanate ion, their extractions were in this case negligible, probably due to the high selectivity for gold and, to a lesser extent, for other metal cyanide complexes exhibited by these extractants.

TABLE 20. Concentrations of free CN^-, SCN^-, and dissolved amine

Cycle or Feed solution	Free CN^- mg/L	SCN^- mg/L	Dissolved Amine, g/L
Campbell	449	351	<0.001
8	426	321	0.012
9	390	396	0.009
10	386	304	0.011
16	385	302	0.004
17	380	289	0.003
Hemlo	270	52	0.003
26	260	50	0.008
27	280	51	0.008
28	270	50	0.008

The low concentration of amine in the raffinates is in agreement with reported values [1]. Therefore, quaternary amines exhibit a lower water solubility than TBP, DBBP and other gold extractants and modifiers [14]. The low water solubility of the quaternary amines is an important aspect from an economic and environmental point of view. For this reason quaternary amines appear to be the best alternative for an industrial application of solvent extraction of gold.

3.4 Stripping

Because of their high affinity for the gold cyanide complex, quaternary amines are not readily stripped. From this point of view, quaternary amines and strong base resins behave similarly. Among the several reagents and procedures that were tested, only a few were found effective and studied in more detail. These were: simultaneous displacement and cementation with zinc cyanide

and metallic zinc, stripping with acidic thiourea solutions and air sparging and incineration of the organic solvent.

3.4.1 Simultaneous displacement and cementation

The displacement of the gold cyanide complex with the zinc complex has been used for the elution of strong base resins [11]. The reaction can be described as:

$$2R_4N^+Au(CN)_2^- + Zn(CN)_4^{2-} = (R_4N^+)_2Zn(CN)_4^{2-} + 2Au(CN)_2^- \quad (3)$$

Because of the strong affinity between quaternary amines and the gold cyanide complex, the displacement of the latter with zinc cyanide is not efficient. Figure 17 presents a stripping isotherm of a loaded 5% Aliquat 336 solution with an aqueous solution of 0.5 M zinc cyanide. The initial loading of the organic phase was: Au 999 ppm, Zn 1960 ppm, Ni 270 ppm, Cu 37 ppm and Fe 0 ppm. Despite the high concentration of zinc cyanide complex the efficiency of the stripping is low. The stripping isotherm shows that a multistage countercurrent process would produce a strip liquor containing only about 50 ppm gold. The concentration increase, with respect to a typical cyanide leach solution, would be of only 5 to 10 times.

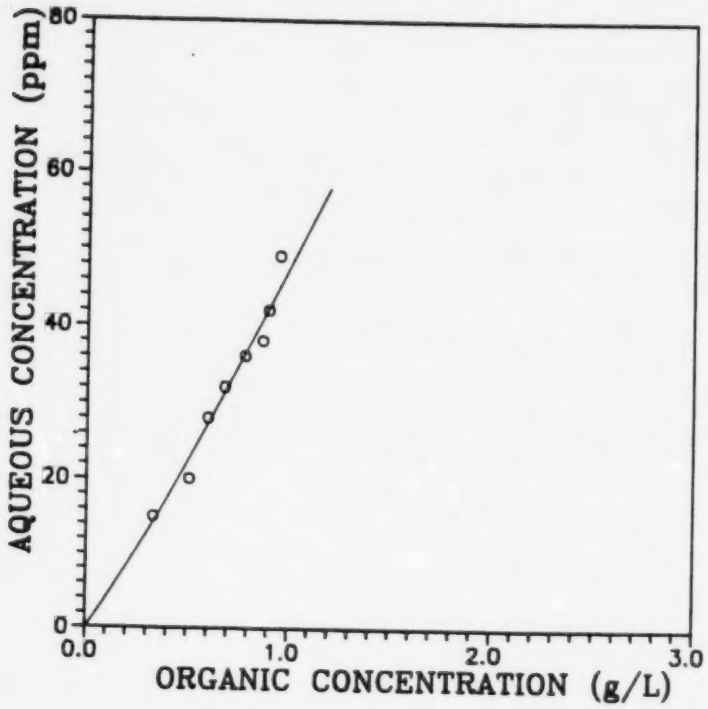

FIGURE 17. Stripping of gold from 5% Aliquat 336 with a 0.5 M zinc cyanide solution.

It was found experimentally that the efficiency of the stripping could be greatly improved by the presence of zinc dust. The effect of the latter is to reduce the gold complex to metallic gold and, thus, to decrease the concentration of gold in the aqueous phase. This, in turn, results in more gold complex coming out of the organic phase to restore the equilibrium. Figure 18 shows that the organic gold concentration of a 20 mL aliquot has been reduced from 805 ppm Au to less than 300 ppm Au by one contact with 3 mL of 0.5 M zinc cyanide in the presence of zinc dust.

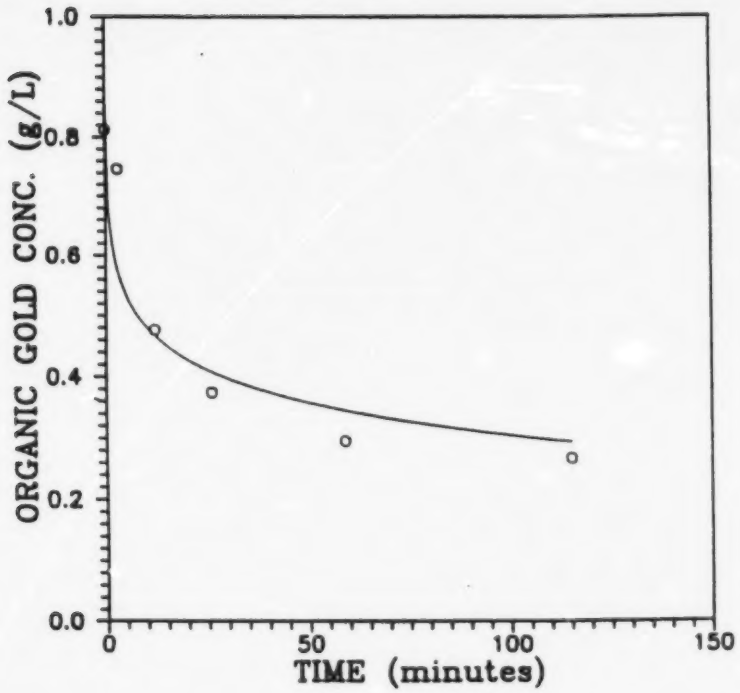

FIGURE 18. Stripping of gold from 5% Aliquat 336 with a zinc cyanide solution in the presence of zinc dust.

One drawback of the displacement-cementation method is that the quaternary amine becomes loaded with zinc cyanide complex. Although several effective ways to remove the zinc cyanide complex from quaternary amines have been described [12], the process becomes complicated due to the need to treat the effluent solutions. For this reason, other stripping methods appear to be simpler. However, it is believed that a process involving simultaneous displacement and cementation of gold with zinc cyanide and zinc dust, followed by the removal of the zinc cyanide from the organic phase is technically feasible.

3.4.2 Stripping of gold with acidic solutions of thiourea

Acidic solutions of thiourea have been used for the elution of gold from strong base resins in the USSR [11]. This method is based on the decomposition of the cyanide complex in an acid medium and the subsequent formation of a positively charged gold-thiourea complex that is not held by the ammonium group. The reaction can be described as follows:

$$R_4N^+Au(CN)_2^- + 2HX + 2CS(NH_2)_2 = R_4N^+X^- + Au(CS(NH_2)_2)_2^+ + X^- + 2HCN \quad (4)$$

The attractive features of this method include: 1) the extractant is completely regenerated and can be recycled directly; and 2) an important amount of free cyanide can be recovered. In the case of strong-base resins, the elution with acidic thiourea presents some operational problems, such as [11]: 1) breakage of the resin beads due to osmotic shock; 2) the precipitation of cobalti- and ferrocyanide compounds in the resin matrix; and 3) the decomposition of thiourea during the electrowinning of gold. In addition, the generation of hydrocyanic acid during the stripping requires special safety precautions.

In the case of quaternary amines, the stripping with acidic thiourea appears to be an attractive route because most of the above-mentioned problems do not arise. Since quaternary amines do not have a rigid matrix and extract almost no iron or cobalt, they are practically immune to both osmotic shock and to the

precipitation of cobalti- and ferrocyanides. Furthermore, since quaternary amines exhibit fast reaction kinetics and high loading capacity for gold, the inventory of loaded organic would tend to be small. This fact would facilitate the operation of a small circuit which is important in order to handle safely the generation of hydrocyanic acid.

Groenewald [3] reported that the stripping of Aliquat 336 with thiourea in hydrochloric acid solutions was inefficient leading to a maximum gold concentration of only 0.68 g/L in the strip liquor. A significant improvement was observed with the use of thiourea in perchloric acid. No information is given, however, about the possible oxidation effect of the perchloric acid on the quaternary amino group or about the need to remove the perchlorate ion before recycling the extractant.

In the present work it was confirmed that solutions of thiourea in hydrochloric or sulphuric acid produced an incomplete stripping of gold. Later it was found that the removal of the hydrocyanic acid, which is generated during the stripping, was essential to attain an efficient stripping of gold. Although HCN is a gas at room temperature, it is also extremely soluble in water and it is evolved from aqueous solutions at a rather slow rate [13]. During the stripping of quaternary amines with acidic thiourea, the generated hydrocyanic acid tends to concentrate in the aqueous phase unless it is removed at a fast rate. If the

HCN reaches a high concentration in the aqueous solution, the stripping of gold from quaternary amines will be incomplete.

It was found experimentally that air sparging was an effective way to remove the HCN from the stripping solution and, at the same time, to promote the mixing of the organic and aqueous phases. The equipment used for the thiourea stripping with air sparging is shown in Figure 19. This consists of a reaction chamber and two reservoirs filled with NaOH to capture the HCN and produce NaCN for recycling. The air stream is forced through the system by applying vacuum.

Figure 20 shows the kinetics of the HCN evolution during the acid stripping with acid solutions and with air sparging. The air flow rate was about 0.5 bed volumes per second. The results demonstrate that HCN is not evolved readily from the aqueous solution since it takes several minutes and intense air sparging to reduce effectively its levels in the reaction chamber. The evolution of HCN is much faster when thiourea is present in the acid solution, which is probably related to the faster decomposition of the cyanide complexes in the presence of this reagent. By contrast, the evolution of HCN proceeds at a slower rate with solutions of mineral acids. The nature and the concentration of the acid do not appear to exert a major effect on the speed of the gas evolution.

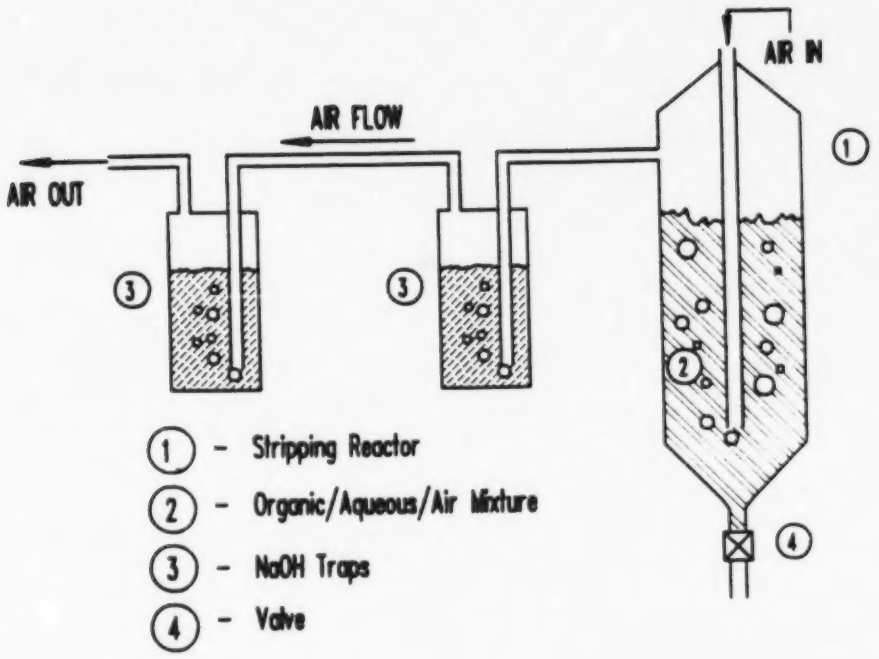

FIGURE 19. Equipment for stripping with acidic thiourea and air sparging.

It was found that solutions of either hydrochloric or sulphuric acid with or without air sparging did not strip significant amounts of gold. However, some of the less stable cyanide complexes were decomposed and this provided a practical means to remove impurities, especially nickel and zinc, from the organic solution before the stripping of gold. It was found that washing with sulphuric acid was effective for removing nickel and zinc but some small amounts of gold were also stripped. On the other hand, washing with hydrochloric acid solutions resulted in

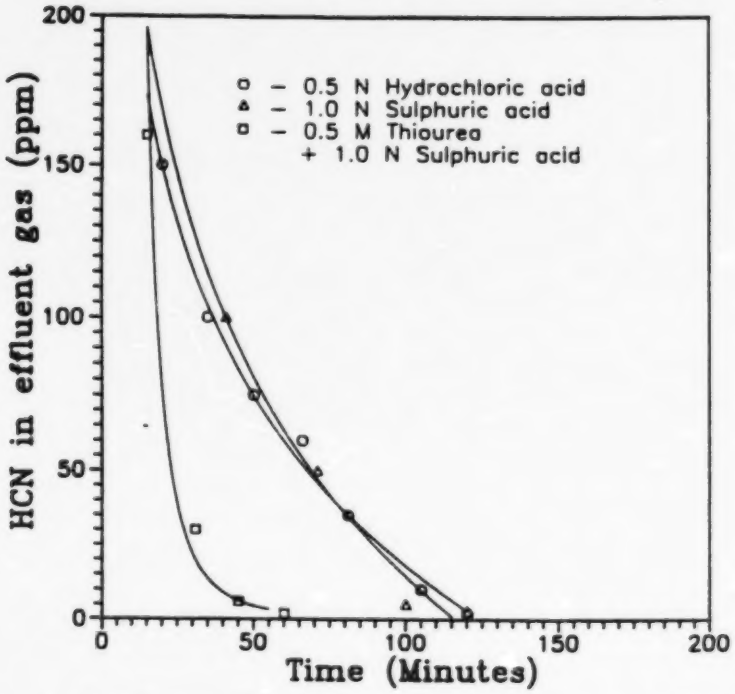

FIGURE 20. Evolution of HCN during acid stripping with air sparging.

the removal of nickel without any stripping of gold, but zinc stayed in the organic phase. The best results for an efficient acid wash with no losses of gold were obtained with a mixture of 0.5 M H_2SO_4 and 0.05 M HCl and air sparging during 2 hours.

As shown in Figure 21, the acid wash of the organic solution (with the sulphuric/hydrochloric mixture described above) has also an important effect on the kinetics of the stripping of Aliquat 336 with acidic solutions of thiourea. Since a considerable amount of HCN has already been evolved during the acid wash, the gold stripping kinetics are faster with the acid-washed organic solution. The fact that the stripping of gold is

slower when the organic has not been washed (and, therefore, the amount of HCN being evolved is larger) gives further support to the idea that the concentration of HCN in the aqueous solution determines the extent of the stripping of gold.

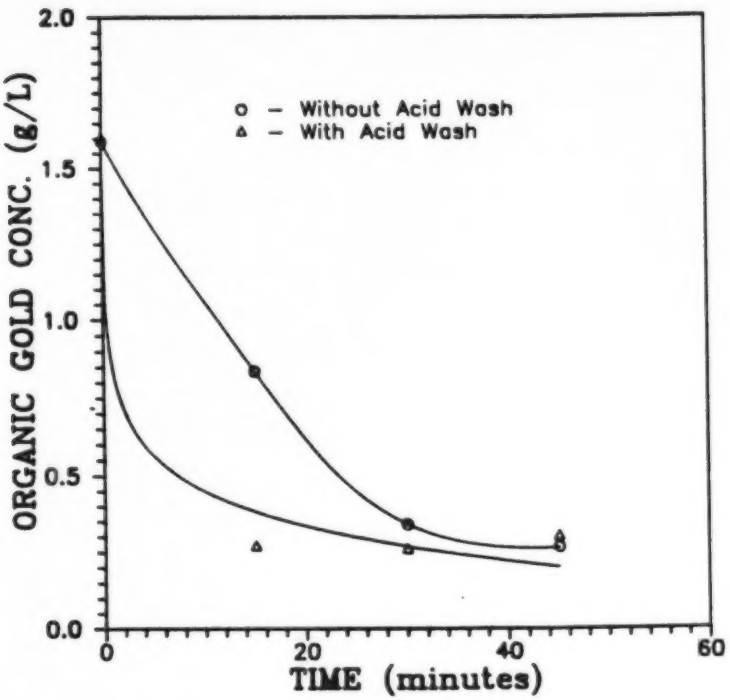

FIGURE 21. Stripping kinetics of 5% Aliquat 336 with acidic thiourea and air sparging.

Once the main variables of the stripping procedure had been determined, it was applied to strip the gold from several samples of organic solutions from the continuous circuit experiment. Two typical experiments are described below:

Experiment 1. A 50 mL sample of 10% Aliquat 336 solution in Solvesso 150 (loaded with the Campbell Red Lake solution) was put into the reaction chamber of the stripping equipment described above. The air sparging was started and a mixture of 0.5 M H_2SO_4 and 0.05 M HCl was added to wash the organic solution. After two hours the concentration of HCN in the effluent air was within safe levels. At this point the acid mixture was removed from the reaction chamber. A solution containing 0.5 M thiourea and 0.5 M sulphuric acid was added to the washed organic solution in the reaction chamber. After 10 minutes of mixing with air sparging, the thiourea solution was removed and some fresh solution of thiourea was added. This last step was repeated several times until no gold was left in the organic phase. The air sparging, at a flow rate rate of 0.5 BV/s, was maintained during the experiment. The analyses of the aqueous and the organic solutions are presented in Table 21 and Table 22 respectively.

TABLE 21. Stripping of 10% Aliquat 336 with 0.5 M thiourea and 0.5 M H_2SO_4. Analysis of the aqueous solutions (mg/L)

Solution	Vol.(mL)	Au	Cu	Zn	Ni	Fe
Acid Wash	25	1	9	6297	578	0
Strip soln. 1	20	3215	110	418	858	0
Strip soln. 2	20	1783	5	265	363	0
Strip soln. 3	20	575	0	180	6	0
Strip soln. 4	20	215	0	140	0	0
Strip soln. 5	20	68	0	99	0	0
Strip soln. 6	20	22	0	74	0	0

TABLE 22. Stripping of 10% Aliquat 336 with 0.5 M thiourea and 0.5 M H_2SO_4. Analysis of the organic solutions (mg/L)

	Vol.(mL)	Au	Cu	Zn	Ni	Fe
Loaded	50	2080	83	3860	578	0
Stripped	--	0	0	218	0	0

Experiment 2. A 50 mL sample of 5% Aliquat 336 solution in Solvesso 150 (loaded with the Teck-Corona Hemlo solution) was used. The same stripping procedure as described above was carried out. The aqueous and organic solutions are presented in Tables 23 and 24 respectively.

TABLE 23. Stripping of 5% Aliquat 336 with 0.5 M thiourea and 0.5 M H_2SO_4. Analysis of the aqueous solutions (mg/L)

Solution	Vol.(mL)	Au	Cu	Zn	Ni	Fe
Acid Wash	25	0	13	12	1615	0
Strip soln. 1	20	5228	110	6	17	0
Strip soln. 2	20	1192	5	8	1	0
Strip soln. 3	20	160	0	6	0	0
Strip soln. 4	20	24	0	7	0	0
Strip soln. 5	20	4	0	6	0	0
Strip soln. 6	20	2	0	7	0	0

TABLE 24. Stripping of 5% Aliquat 336 with 0.5 M thiourea and 0.5 M H_2SO_4. Analysis of the organic solutions (mg/L)

	Vol.(mL)	Au	Cu	Zn	Ni	Fe
Loaded	50	2228	55	137	734	0
Stripped	--	0	0	111	0	0

These results demonstrate that the stripping of gold from quaternary amines with acidic thiourea and air sparging is effective. The organic solution is completely depleted of gold after the stripping procedure. The acid wash is effective in removing significant amounts of impurities such as zinc and nickel. Therefore, the strip liquors, that with the appropiate recycling could attain several grams per litre of gold, are not heavily contaminated and should produce a high purity final product.

The recovery of gold from the thiourea solution has previously been studied [18]. It is believed that gold could be readily recovered by eletrowinning or precipitation. Due to the high concentrations of gold in the strip liquor the possible losses of thiourea during the electrowinning or precipitation would be only a minor factor on the overall economics of the process.

3.4.3 Incineration of the organic solvent

The experimental results show that, in some cases, a 5% Aliquat 336 solution could load as much as 2.5 g Au/L. Therefore, the gold is dissolved in an organic phase whose composition

is close to 95% of diluent. If all of the diluent was removed from the system by distillation, the concentration of gold in the residue would be 50 g/L. Because of the high concentration of gold in this reduced volume of residue, it was thought that incineration could be a viable alternative for recovering the gold. Although quaternary amines are relatively expensive reagents, their cost is only a small fraction of the value of the gold contained.

Incineration has been practiced sporadically to recover gold from activated carbon. In this case the procedure is not very attractive, however, because the activated carbon requires high temperatures which can only be attained with the use of external fuel, and a long incineration time. Under those drastic conditions, some contaminating metals can be reduced to the metallic state and mix with the gold.

By contrast, quaternary amines are liquid hydrocarbon compounds that burn readily at low temperatures (less than 800°C). Therefore the few base metals that are extracted by these reagents are unlikely to be reduced to the metallic state. The metal with more chances of becoming reduced during incineration is copper, which is not loaded to a major extent by the quaternary amines. Zinc and nickel are unlikely to be reduced to the metallic state. Thus the gold product from the incineration can be expected to be of high purity.

Several samples of loaded organic from the continuous circuit were subjected to distillation and incineration to demonstrate the technical feasibility of the procedure. Solvesso 150 distilled readily below 100°C under vacuum and the separation from Aliquat 336 was complete. The liquid residue (loaded Aliquat 336) burned gently without the application of external heat. No losses of gold were detected during the procedure. The solid residue from the incineration was analyzed by X-ray diffraction and scanning electron microscope. The only elements found were metallic gold, nickel oxide, zinc oxide and silica. Hot dilute nitric acid removed readily the zinc and the nickel from the solid residue. The remainder was melted in a furnace at 1100°C to produce clean round particles of high-purity gold.

Future research will deal with the economical aspect of the incineration process as compared with the other alternative recovery methods. Although replacing Aliquat 336 on a continuous basis would appear to be an expensive procedure, this has to be weighed against the potential advantages that the method would introduce as compared with conventional technology. These would include: 1) elimination of electrowinning or precipitation; 2) faster gold output and reduction of gold inventory; and 3) the production of high-purity gold. One potential way to reduce the reagent cost of the incineration process would be to use quaternary amines of a technical grade. Whether these technical grade

quaternary amines would exhibit the same chemical and physical characteristics would have to be evaluated with additional test-work.

4. CONCLUSIONS

The feasibility of extracting gold efficiently from clarified cyanide solutions in a continuous circuit using a quaternary amine has been demonstrated. The use of an aromatic diluent such as Solvesso 150 prevented effectively the formation of emulsions and crud.

Quaternary amines exhibited superior overall characteristics than other solid and liquid gold extractants with respect to selectivity and loading capacity. They also exhibited low water solubility, good phase separation and a moderate sensitivity to the ionic strength of the aqueous phase. Because of this adequate combination of physical and chemical characteristics, quaternary amines such as Aliquat 336 and Adogen 483, appear to be the best choice for the development of a solvent-in-pulp process. Their highest potential may be in the recovery of gold from pulps and solutions highly contaminated with other elements, in which conventional methods have proved to be less effective.

The stripping of gold from quaternary amines can be done with acidic solutions of thiourea and air sparging. Because of their fast kinetics and high capacity, quaternary amines can be

stripped in a relatively small circuit which facilitates taking the necessary safety precautions during this operation.

Under favourable conditions, high loadings of gold can be obtained. In these cases, the recovery of gold can be done by incinerating the organic solvent. The best procedure would probably be to distil off the diluent to produce a residue for incineration having a concentration of 50 g Au per L. Since quaternary amines are selective for gold, the contamination of the incinerated product is small. Because of the low temperatures needed for the incineration, any base metals present in the residue are not reduced to the metallic state. This fact facilitates the cleaning of the final product and opens the interesting possibility of producing high-purity gold. An aspect that should be explored is the use of technical grade quaternary amines with the purpose of lowering the reagent cost.

The results reported in this work indicate that the solvent extraction of gold from clarified solution with quaternary amines is a viable process and in some cases could offer important advantages over the conventional technology in terms of kinetics, selectivity and loading. One potential area of application for solvent extraction of gold could be in conjunction with the heap leaching process. This increasingly popular technique produces clarified solutions and would benefit from the reduction in

solution volume resulting from the faster reaction kinetics of solvent extraction.

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